

Concentrations of Organic Contaminants in Mollusks and Sediments at NOAA National Status and Trend Sites in the Coastal and Estuarine United States

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Mean concentrations of PAHs, PCBs, and DDT in mollusks and sediments at sites in the National Status and Trends Program (NST) are distributed in log-normal fashion. The dry weight-based chlorinated organic concentrations in mollusks generally exceed those in nearby sediments by an order of magnitude. PAHs are found at similar concentrations in sediments and mollusks. Highest concentrations of PCBs and DDT in mollusks are in the ranges of 1000 to 4000 ng/g (dry) and 400 to 1000 ng/g (dry), respectively. The highest PAH concentrations in sediments are in the 10,000 to 50,000 ng/g (dry) range. While higher concentrations of contaminants can be found by sampling localized hot spots, the NST data represent the distribution of concentrations over general areas of the coastal United States.

Introduction

The National Status and Trends (NST) Program of the National Oceanic and Atmospheric Administration (NOAA) monitors chemical contamination and biological responses to contamination in the coastal and estuarine United States. The program has two main parts: the Benthic Surveillance Project and the Mussel Watch Project. Benthic surveillance began in 1984 with the collection of surface sediments and benthic fish at 50 sites around the United States, and mussel watch began in 1986 with the collection of bivalve mollusks (mussels and oysters) and surface sediments at 150 sites. Since then, more sites have been added to each project.

Data on concentrations of 17 elements and 50 organic compounds have been obtained in mollusks on an annual basis and on a less frequent basis in fish livers and surface sediments. Results have been presented and discussed in a series of reports (1-3). Discussion here is limited to concentrations in mollusks and sediments of DDT, polychlorinated biphenyls (PCBs), and polycyclic aromatic hydrocarbons (PAHs); classes of compounds included among suspected or known carcinogens (4).

Sites

Sites occupied by the Benthic Surveillance and Mussel Watch Projects through 1988 are listed and located on maps in NOAA (2,3). The average distances between sites are 20 km in estuaries and embayments and 100 km along open coastlines. The sites have been selected with the intention of collecting samples that are

representative of their surroundings. Small-scale patches of contamination and known points of waste discharge have been avoided.

Sediment has been collected at three stations within each site, a station being anywhere within 500 m of a site center. In the Mussel Watch Project, if only sand could be found at a mollusk site, the sediment site could be as much as 2 km away. For benthic surveillance sampling in the Northeast, stations were approximately 5 km apart, so, in effect, a site could be 100 times larger than that for other NST sites. Sediment samples have been obtained with specially constructed box covers, Smith-MacIntyre bottom grabs, or Van Veen grab samplers. Subsamples for organic analyses have been surface skims from the top 3 cm (benthic surveillance) or 1 cm (mussel watch) of each grab or core. Composites have been made by mixing samples from three cores or grabs at each station and, in turn, three composites have been analyzed per site per year.

Six laboratories have provided NST organic chemical data: the NOAA National Marine Fisheries laboratories in Seattle, Washington, Charleston, South Carolina, and Gloucester, Massachusetts; the Battelle Ocean Sciences Laboratory in Duxbury, Massachusetts; the Science Applications International Corporation laboratory in La Jolla, California; and the Texas A & M Geochemical and Environmental Research Group in College Station, Texas. The methods by which chlorinated compounds and PAHs have been extracted from sediments and subsequently analyzed have been based on those detailed in MacLeod et al. (6). Wade et al. (7) describe methods slightly different from those of MacLeod, but nevertheless, the methods are acceptable on the basis of comparable results. Intercalibration exercises continue as part of the NST Program. Results of intercalibrations through 1987 are included in MacLeod (8).

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Consolidation of Chemical Data

The PAH compounds considered in this report are the 18 listed in Figure 1. Total PAH (tPAH) in this context is the sum of the 18 concentrations. Two subsets of tPAH are the low molecular weight (LMWPAH) and the high molecular weight (HMWPAH) compounds, which are those with two and three rings, and with four and five rings, respectively. Data for concentrations of PCB compounds have been aggregated to total PCBs (tPCB). It is the sum of concentrations at each level of chlorination or, equivalently, in the case of 1988 data for mollusks, twice the sum of the concentrations of 18 PCB congeners (3). Total DDT (tDDT) is the sum of the concentrations of the parent compound and its metabolites (primarily *p,p'* DDE and *p,p'* DDD).

Data for concentrations in mollusks collected from 1986 to 1988 have been combined without regard to year. This conflicts with the NST mission of monitoring temporal trends in contamination. It is, in fact, the mollusk data that will serve as the basis for defining such trends. This is especially so with organic chemical data that display more within-year variability than elemental data. Of the 177 sites from which mollusks have been collected, 136 have been sampled in each of 3 years, 12 sampled in 2 years, and 29 sampled in only 1988. In general, mean concentrations reported here are based on 9 determinations.

Data for concentrations in sediments collected from 1984 to 1985 (benthic surveillance sites) or from 1986 to 1987 (mussel watch sites) have been combined. Unlike mollusks that can adjust contaminant burdens in response to changes in the surroundings, sediment data are not expected to reflect annual conditions. In fact, sediment data are no longer being collected annually. In general, mean concentrations are based on six determinations (three per year). Because contaminants are associated with surface particles, sediment data have been modified in two ways to remove the influence of particle size on concentrations. First, data have not been used from sediment samples that contained more than 80% sand-sized ($> 63 \mu\text{m}$) particles. Second, all data have been normalized by dividing by the fraction of particles that are silt or clay ($< 63 \mu\text{m}$).

Distribution of Concentrations between Mollusks and Sediments

Spearman ranked correlation coefficients between data for sediment and mollusks from the 117 sites where fine-grained sediment and mollusks were collected in 1986 and 1987 are 0.68, 0.70, 0.62, 0.50, and 0.60 for tPCB, tDDT, tPAH, LMWPAH, and HMWPAH, respectively. All of those coefficients are significant at the 0.01 level and imply that, in general, mollusks from sites with high or low concentrations in fine sediment will display correspondingly high or low concentrations of those compounds.

Although they follow one another, dry-weight-based concentrations of tPCB and tDDT have been much higher in mollusks than in nearby sediments. For tPAH this is not the case. For the 117 sites that yielded both mollusks and fine-grained sediment in 1986 and 1987, the average ratios of mollusk:sediment concentrations were 9.1 for tPCB and 22 for tDDT, but only 1.2 for tPAH, 2.0 for LMWPAH and 0.64 for HMWPAH. Differences in octanol water coefficients do not seem sufficient to explain these differences, and physical/chemical characteristics alone cannot account for the lower HMWPAH ratio compared to the

LMWPAH ratio. Perhaps there is a biological breakdown of PAH occurring in mollusks. The metabolism of PAH compounds in teleosts has been well demonstrated, and intermediate compounds created in this process may be active carcinogens (9,10). It is because of this metabolic loss that PAHs are not being monitored in fish livers.

There is an overall correspondence between sediment and molluscan concentrations for tPAH, but mollusks tend to have higher concentrations of two-ring compounds, while sediments have higher levels of the five-ring compounds benzo(a)- and benzo(e)pyrene, perylene, and dibenz(a,h)anthracene (Fig. 1). The two-ring compounds are the more soluble of the PAHs and the more likely to be found in episodic discharges of petroleum. The relatively high solubility of two-ring compounds may prevent their accumulation in sediments and allow only mollusks to reflect the ephemeral nature of their inputs. The higher molecular weight compounds, on the other hand, are generated from the combustion of fossil fuels and have chronic nonpoint sources to the marine environment. The relative absence of high molecular weight compounds in mollusks is not readily explained unless mollusks can metabolize such compounds.

Concentrations of Organic Contaminants in Mollusks and Sediments

Because mollusks have higher concentrations of tDDT and tPCB than sediments, molluscan data have been chosen to illustrate the nationwide distribution of concentrations. Figures 2 and 3 show the high and low ends of the approximately log-normal distributions of tDDT and tPCB, respectively. The site locations are identified, and to distinguish among sites in a general area, site codes are also shown. Four- and three-letter codes signify mussel watch and benthic surveillance sites, respectively. General and specific site identifiers and codes are provided, along with maps, in NOAA (2,3).

The U.S. Food and Drug Administration (FDA) recommends against human consumption of seafood containing more than 5000 and 2000 ng/g (wet weight), respectively, of tDDT and tPCB. Assuming mollusks to be 80% water (actually the mean is closer to 85%), the corresponding dry weight concentrations would be 25,000 and 10,000 ng/g. These concentrations are more than the highest concentrations in mollusks at NST sites. The NST sites were chosen to represent relatively large areas and are deliberately not near known point sources of contamination. The fact that the highest concentrations found are not above FDA levels does not mean that no mollusks in the coastal United States would exceed those levels. It does, however, indicate that such mollusks, if found, would be very locally distributed.

The distribution of tPAH concentrations is demonstrated with sediment data in Figure 4. As with the tPCB and tDDT data, the highest concentrations are primarily in the urban areas. Again, the data are not intended to include the highest possible concentrations. The highest value on Figure 4 is 58,000 ng/g dry and may be atypical of Boston Harbor. Other sites in Boston Harbor also have relatively high tPAH levels, but are less than 10,000 ng/g. Even the high value, however, is not as high as some of those reported by Shiaris and Jambard-Sweet (11), who analyzed a similar suite of PAH compounds in sediments from the inner parts of Boston Harbor and around the piers. Other hot spots

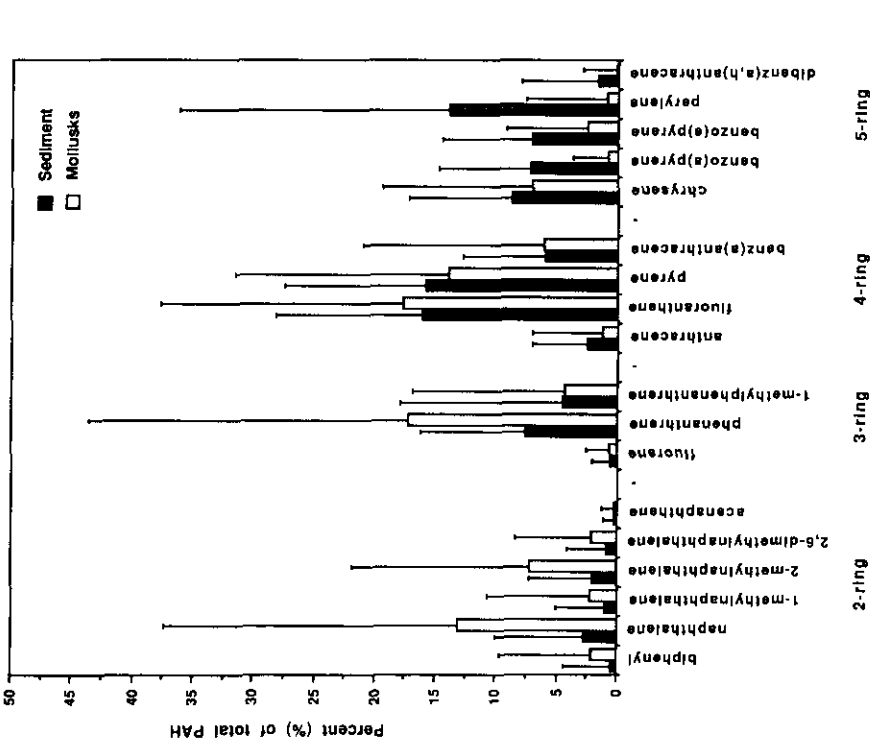


FIGURE 1. Average percentage (+ SD) contribution of each compound to total PAH concentration in sediments (n = 1032) and mollusks (n = 990) for all samples in the National Status and Trends database.

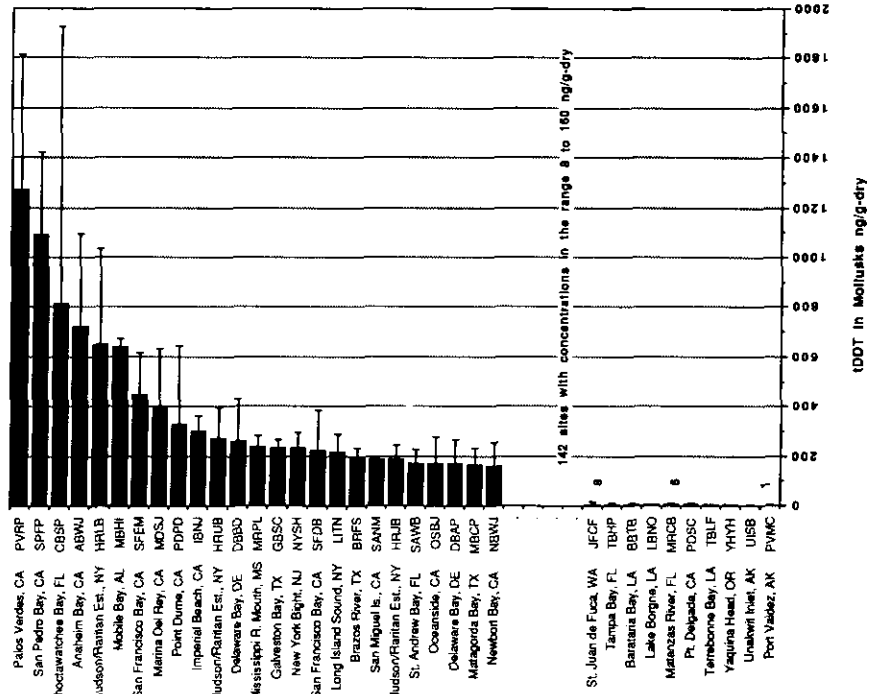


FIGURE 2. Concentrations (+ SD) of DDT in mollusks collected from 1986 through 1988. The number of samples per site is three per year, and since years have been combined, each concentration is generally the mean of nine. Values are shown for three of the lowest concentrations because on the scale of the figure the bars for the lowest concentrations cannot be seen.

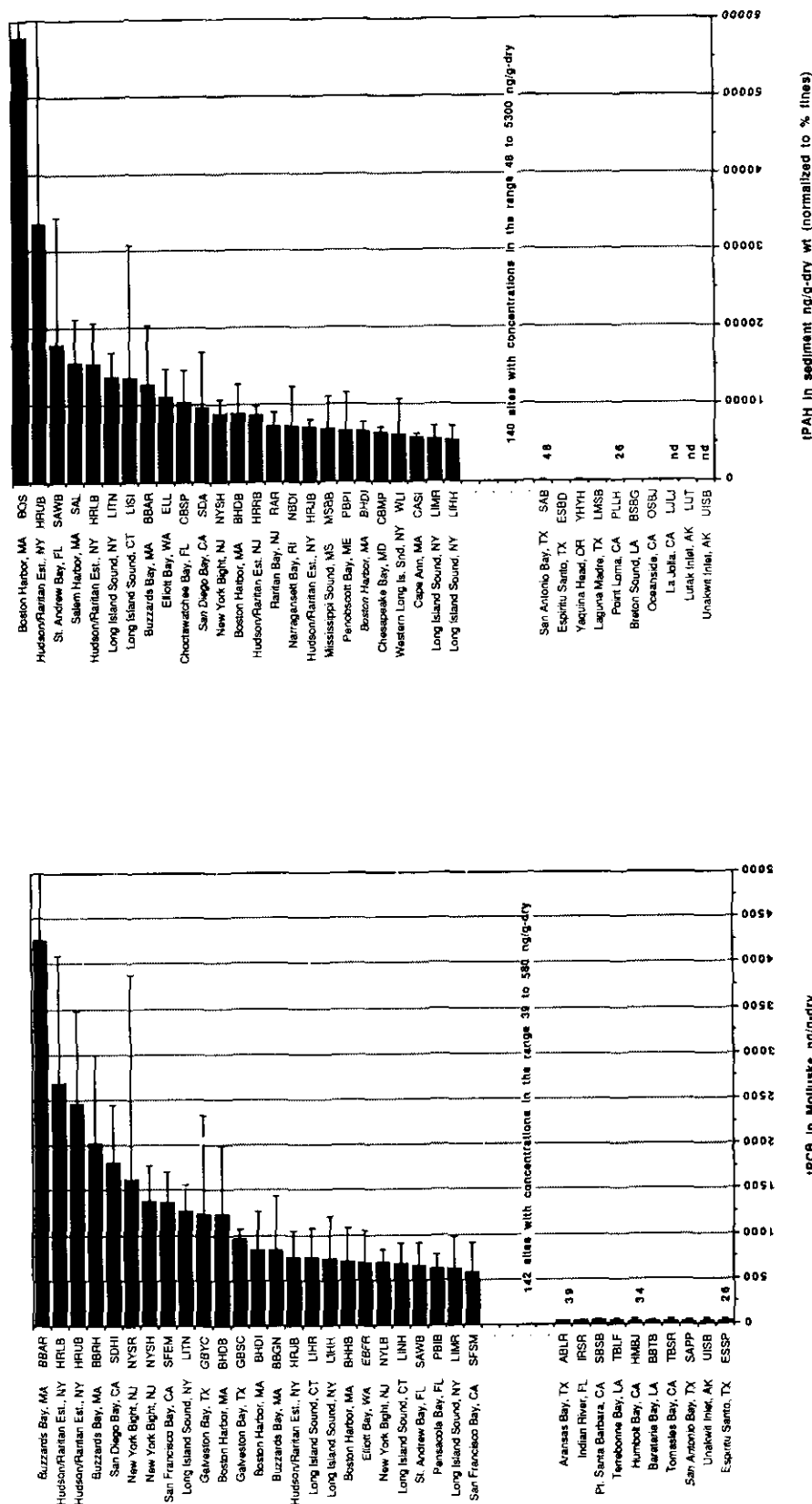


FIGURE 3. Concentration (+ SD) of tPCB in mollusks collected from 1986 through 1988. The number of samples per site is three per year, and since years have been combined, each concentration is generally the mean of nine. The standard deviation for the highest concentration (site BBAR) has not been entirely included. It is ± 2200 ng/g. Values are shown for three of the lowest concentrations because on the scale of the figure the bars for the lowest concentrations cannot be seen.

FIGURE 4. Concentrations (+ SD) of tPAH in sediments collected in 1986 and 1987. Concentrations have been normalized to the fraction of sediment finer than $63 \mu\text{m}$. Data were not used if that fraction was less than 0.2. The number of samples per site is three per year, and since years have been combined, each concentration is generally the mean of six. The standard deviation for the two highest concentrations (sites BOS and HRUB) have not been entirely included. They are $\pm 43,000$ and $\pm 28,000$ ng/g, respectively. Values are shown for three of the lowest concentrations because on the scale of the figure the bars for the lowest concentrations cannot be seen.

such as those in the industrial waterways of Seattle and Tacoma in Washington State (12) and the Elizabeth River near Portsmouth, VA (13), also contain sediments with tPAH concentrations in excess of 50,000 ng/g. There are many NST sites in Southern California and several appear in Figure 2 because of high tDDT concentrations in mollusks, but few have high tPAH concentrations in sediments. Concentrations in excess of 10,000 ng/g have been found near industrialized locations (14).

Conclusions

Excluding the five highest and lowest concentrations, one finds that in mollusks the concentrations of tPCB, tDDT, and tPAH at NST sites span about two orders of magnitude. The spans for sediment concentrations are slightly greater for tPAH and tPCB and reach a factor of 1000 for tDDT. For the chlorinated organic compounds, concentrations in mollusks exceed those in sediments by about 10-fold, while for tPAH, sediments and mollusks have similar concentrations. The highest concentrations at NST sites represent high values for a general survey of the coastal and estuarine United States but are exceeded at local hot spots.

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